b

(NASA Contract NASw-6)
indef only N-98625 4087
(NASA CR-55117; JPL-TR-32-100)

Technical Report No. 32-100

N63-86431
Code 5

General Theory of Collision-Broadening of Spectral Lines

Oldwig von Roos 20 Apr. 1961 14p refs

474 2003

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

April 20, 1961

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
CONTRACT NO. NASw-6

Technical Report No. 32-100

General Theory of Collision-Broadening of Spectral Lines

Oldwig von Roos

Frank B. Estabrook

Frank B. Estabrook, Chief
Physics Section

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

April 20, 1961

CONTENTS

GENERAL THEORY OF COLLISION BROADENING OF SPECTRAL LINES[1]

O. H. von Roos

ABSTRACT

A quantum-mechanical theory of spectral line broadening is developed. The theory incorporates Doppler broadening and collision broadening in a natural way. Working in the interaction representation with respect to the collisional degrees of freedom and taking inelastic collisions fully into account, general formulas are derived for the line shift, the line breadth, and the line shape of an optical spectral line of an arbitrary quantum-mechanical system provided that the line breadth is small compared to the emitted frequency and that the final state is stable (ground state).

I. INTRODUCTION

Generally there are two different methods available for dealing with theoretical investigations of the influence of collisions on the shape and shift of spectral lines. These are the impact theory (Ref. 1, 2) and the statistical theory (Ref. 1-4). The two methods start with very different assumptions. In the impact theory one assumes that collisions divide the wave of an emitting atom abruptly into incoherent wave trains, resulting in the broadening. In the statistical theory one assumes that perturbing neighbors induce a Stark effect and therefore change the frequency of the emitting atom; then the probability that this frequency lies between w and $w + dw$ determines the shape of the spectral line. Excellent review articles on the subject are available (Ref. 5).

[1] This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract NASw-6, sponsored by the National Aeronautics and Space Administration.

It is somewhat surprising, however, that there does not seem to be a *general* recipe of how to calculate spectral line shapes at least in principle. The situation is quite different in the field of atomic collisions (Ref. 6). Here there is a general theory for binary collisions which is applicable to all kinds of situations: elastic or inelastic collision, low or high impact energies, etc. Although for moderately complex systems the algebra involved in calculating cross sections may be formidable, at least in principle the computations can be done and the results will agree with experiment. Unfortunately the same cannot be said of theories of spectral line broadening.

On the other hand, the well-established theory of the natural line width (Ref. 7) does not have any of the above mentioned difficulties and as such is quite generally applicable for an isolated atom. In this paper a theory of line broadening will be given which uses the general theory of collisions as given in Ref. 6 and combines it with the theory of the natural line width (Ref. 7) to yield a formula for the line shape, etc., which is applicable for a wide variety of problems. At the same time photon recoil will be incorporated. Since this is tantamount to incorporating the Doppler effect it is possible to investigate the interplay between the Doppler effect and collision broadening (Ref. 8).

In particular, the theory will be developed which will ultimately lead to formulas for the line shape, the line width and the line shift. Subsequently, it will be shown that the formula for the line shape may be cast into a form which is essentially equivalent to the formula of the line shape as given by the correlation function theory (Ref. 9).

II. DEVELOPMENT OF THE THEORY

Consider two quantum mechanical systems characterized by their respective hamiltonians $H_1(\mathbf{r}_1)$ and $H_2(\mathbf{r}_2)$. $\mathbf{r}_1$ as well as $\mathbf{r}_2$ stands for a collection of electron coordinates, as many as are needed to specify the systems. If the electrostatic interaction is introduced, as well as the interaction with the radiation field, the starting point may be the following Schrödinger equation:

$$\left\{ - \frac{\hbar^2}{2M} \nabla^2_{R_S} - \frac{\hbar^2}{2\mu} \nabla^2_R + H_1(\mathbf{r}_1) + H_2(\mathbf{r}_2) + \phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) + \hbar c \sum_{\alpha, k} k a_k^{(\alpha)\dagger} a_k^{(\alpha)} \right.$$
$$\left. - \frac{e}{mc} \left[\mathbf{A}\left(\mathbf{R}_S - \frac{\mu}{M_1}\mathbf{R} + \mathbf{r}_1\right) \cdot \mathbf{p}_1 + \mathbf{A}\left(\mathbf{R}_S + \frac{\mu}{M_2}\mathbf{R} + \mathbf{r}_2\right) \cdot \mathbf{p}_2 \right] \right\} \psi = i\hbar\dot{\psi} \tag{1}$$

Here $\mathbf{R}_S$ is the coordinate of the center of mass of the two systems under consideration, $\mathbf{R}$ is the relative distance, $M = M_1 + M_2$ is the total mass, $\mu = M_1 M_2/M_1 + M_2$ the reduced mass, ϕ is the electrostatic interaction potential which depends on the relative distance $\mathbf{R}$. The last term on the left side of Eq. (1) signifies the coupling between the radiation field, the latter given by the next to last term, and the electrons. $\mathbf{A}(\mathbf{r})$ is the vector potential and is given by:

$$\mathbf{A}(\mathbf{r}) = \left(\frac{\hbar c}{2V}\right)^{1/2} \sum_{\alpha, k} k^{-1/2} e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{e}_k^{(\alpha)} \left(a_k^{(\alpha)} + a_{-k}^{(\alpha)\dagger}\right) \tag{2}$$

where V is the quantization volume, $\mathbf{k} = k\mathbf{e}_k$ the photon wave vector $\mathbf{e}_k^{(\alpha)}$ a unit vector in one of the two directions of polarization ($\alpha = 1, 2$) so that

$$\mathbf{e}_k \cdot \mathbf{e}_k^{(\alpha)} = 0 \tag{3}$$

and $a_k^{(\alpha)\dagger}$ and $a_k^{(\alpha)}$ are the usual photon creation and destruction operators.

Define

$$H = T_S + H_0 + \phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) \tag{4}$$

$$T_S = -\frac{\hbar^2}{2M}\nabla^2_{R_S} \tag{5}$$

$$H_0 = H_1(\mathbf{r}_1) + H_2(\mathbf{r}_2) - \frac{h^2}{2\mu}\nabla^2_R \tag{6}$$

and transform Eq. (1) into the interaction representation according to:

$$\psi = U\phi = \exp\left(-\frac{it}{h}H\right)\phi \tag{7}$$

Inserting Eq. (7) into Eq. (1) we find that ϕ has to satisfy:

$$i\hbar\dot{\phi} = \left\{ hc \sum_{\alpha, k} k\, a_k^{(\alpha)\dagger} a_k^{(\alpha)} - \frac{e}{mc} U^\dagger \left[\mathbf{A}\left(\mathbf{R}_S - \frac{\mu}{M_1}\mathbf{R} + \mathbf{r}_1\right)\cdot \mathbf{p}_1 + \mathbf{A}\left(\mathbf{R}_S + \frac{\mu}{M_2}\mathbf{R} + \mathbf{r}_2\right)\cdot\mathbf{p}_2\right] U \right\}\phi \tag{8}$$

So far Eq. (8) is still exact. The first approximation is now introduced; ϕ is written as an expansion into zero- and one-photon amplitudes, neglecting all states containing more than one photon (first Tamm-Dancoff approximation):

$$\phi = \phi_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}, \mathbf{R}_S, t)\,\Omega_0 + \sum_{\alpha, k} \phi_\alpha(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}, \mathbf{R}_S, t; \mathbf{k})\,\Omega_1^\alpha(\mathbf{k})\, e^{-itck} \tag{9}$$

In expression (9), Ω_0 is the vacuum state and $\Omega_1^\alpha(\mathbf{k})$ the one-photon state with specified photon momentum $\hbar\mathbf{k}$ and polarization α. Inserting Eq. (9) into Eq. (8) yields two equations for ϕ_0 and $\phi_\alpha(\mathbf{k})$. They are:

$$i\hbar\dot{\phi}_0 = -\frac{e}{mc}\left(\frac{\hbar c}{2V}\right)^{1/2} \sum_{\alpha, k} k^{-1/2}\, U^\dagger D_\alpha^+(\mathbf{k})\, U\phi_\alpha(\mathbf{k})\, e^{-itck} \tag{10}$$

and

$$i\hbar\dot{\phi}_\alpha(\mathbf{k}) = -\frac{e}{mc}\left(\frac{\hbar c}{2V}\right)^{1/2} k^{-1/2}\, U^\dagger D_\alpha^-(\mathbf{k})\, U\phi_0 \tag{11}$$

In Eq. (10) and (11) the operators $D_\alpha^\pm$ are defined by:

$$D_a^{\pm}(\mathbf{k}) = \exp\left[\pm ik\cdot\left(\mathbf{R}_S - \frac{\mu}{M_1}\mathbf{R} + \mathbf{r}_1\right)\right]\mathbf{e}_k^{(a)}\cdot\mathbf{p}_1 + \exp\left[\pm ik\cdot\left(\mathbf{R}_S + \frac{\mu}{M_2}\mathbf{R} + \mathbf{r}_2\right)\right]\mathbf{e}_k^{(a)}\cdot\mathbf{p}_2 \tag{12}$$

The system of equations (10, (11) has to be solved subject to certain initial conditions. Present interest being the spontaneous emission of light, take the condition:

$$\phi_a(\mathbf{k}) = 0 \qquad \text{at } t = 0 \tag{13}$$

i.e., no photon present prior to $t = 0$. For the initial condition on ϕ_0, take the following

$$\phi_0 = \psi_0 \qquad \text{at } t = 0 \tag{14}$$

where ψ_0 is a suitable solution of the stationary Schrödinger equation:

$$[T_S + H_0 + \phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R})]\,\psi_0 = E_0\,\psi_0 \tag{15}$$

Since Eq. (15) conserves total momentum,

$$\psi_0 = e^{i\mathbf{K}_S\cdot\mathbf{R}_S}\,\overline{\psi}_0 \tag{16}$$

with

$$\{H_0 + \phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R})\}\,\overline{\psi}_0 = E_0'\,\overline{\psi}_0 \tag{17}$$

$$E_0' = E_0 - \frac{h^2 K_S^2}{2M} \tag{18}$$

For $\overline{\psi}_0$, take a complete scattering state uniquely defined by asymptotic conditions. Assume for instance that system 1 is in its ground state and system 2 in an excited state characterized by a collection of quantum numbers l. It is then possible to expand $\overline{\psi}_0$ into a complete set:

$$\overline{\psi}_0 = \sum_{n,m} F_{nm}(\mathbf{R})\,\zeta_n(\mathbf{r}_1)\,\zeta_m(\mathbf{r}_2) \tag{19}$$

where

$$H_1(\mathbf{r}_1)\,\zeta_n(\mathbf{r}_1) = E_n^{(1)}\,\zeta_n(\mathbf{r}_1) \tag{20}$$

and

$$H_2(\mathbf{r}_2)\,\zeta_m(\mathbf{r}_2) = E_m^{(2)}\,\zeta_m(\mathbf{r}_2) \tag{21}$$

The wave functions for the relative motion F_{nm} describe the elastic and inelastic scattering processes. They are solutions of their respective equations which may be obtained by inserting the expansion (19) into Eq. (17), supplemented by the following boundary conditions for large R:

$$F_{nm} \sim f_{nm}(\theta)\,\frac{e^{iK_{nm}R}}{R} \tag{22}$$

$$F_{0l} \sim e^{i\mathbf{K}\cdot\mathbf{R}} + f_{0l}(\theta)\,\frac{e^{iKR}}{R} \tag{23}$$

The asymptotic conditions (22) and (23) describe a situation in which we have an incoming plane wave for the relative motion of the two systems under consideration, system 1 being in its ground state, system 2 being in the excited state l. From the amplitudes $f_{nm}(\theta)$ one may derive the inelastic and elastic cross sections in a well-known manner (Ref. 6). In Eq. (22) and (23) K and K_{nm} are defined by:

$$\left.\begin{aligned} \frac{\hbar^2 K^2}{2\mu} &= T \\ \frac{\hbar^2 K_{nm}^2}{2\mu} &= E_0' - E_n^{(1)} - E_m^{(2)} \end{aligned}\right\} \tag{24}$$

where T is the kinetic energy of relative motion which is fixed by experimental conditions and

$$E_0' = T + E_0^{(1)} + E_e^{(2)} \tag{25}$$

At this point, a remark about normalization in the continuum is in order. It is convenient to enclose the system under consideration into a large box of volume V in which case the incoming plane wave is normalized to $V^{-1/2}\,e^{i\mathbf{K}\cdot\mathbf{R}}$ and the density of particles is V^{-1} so that density dependent quantities will easily be identified by their dependence on V.

Of course, other methods of dealing with the scattering problem Eq. (17) than the one outlined above may be employed as well. For instance, if the kinetic energy of relative motion is small the perturbed stationary-state method has to be applied (Ref. 6), etc. But whatever the case may be, ψ_0 may be assumed to be known in the following.

For the solution of Eq. (10) and (11) it is now appropriate to make the ansatz:

$$\phi_0 = e^{-\frac{1}{2}\Gamma t}\,\psi_0 \tag{26}$$

in analogy with the procedure of Ref. 7. It is assumed, in other words, that due to the possibility of a spontaneous emission of system 2 the initial state will decay. It is also appropriate to introduce the complete set of wave functions defined by

$$\left.\begin{aligned} H\psi_E &= E\psi_E \\ \langle\psi_{E'}|\psi_E\rangle &= \delta_{E'E} \end{aligned}\right\} \tag{27}$$

It is not necessary to know anything about these wave functions other than that they form a complete set, both continuous and, if bound states are possible, discrete. Naturally, ψ_0 belongs to this set. Expanding:

$$\phi_\alpha = \sum_E b_\alpha(E, \mathbf{k}, t)\,\psi_E \tag{28}$$

and inserting Eq. (26) and (28) into (11):

$$\begin{aligned} i\hbar\, b_\alpha(E, \mathbf{k}, t) = &-\frac{e}{mc}\left(\frac{\hbar c}{2V}\right)^{\frac{1}{2}} k^{-\frac{1}{2}} \langle\psi_E|D_\alpha^-(\mathbf{k})|\psi_0\rangle\, \frac{\hbar}{i}\left(E - E_0 + \hbar c k - \frac{\hbar}{2i}\Gamma\right)^{-1} \\ &\times\left\{\exp\left[\frac{it}{\hbar}\left(E - E_0 + hck - \frac{\hbar}{2i}\Gamma\right)\right] - 1\right\} \end{aligned} \tag{29}$$

which satisfied the initial condition (13). Together with (26) and (29), Eq. (10) gives an equation for Γ:

$$\begin{aligned} i\frac{\hbar}{2}\Gamma = &\left(\frac{e}{mc}\right)^2 \frac{\hbar c}{2V} \sum_{\alpha, k, E} k^{-1} \langle\psi_0|D_\alpha^+(\mathbf{k})|\psi_E\rangle \langle\psi_E|D_\alpha^-(\mathbf{k})|\psi_0\rangle \left(E - E_0 + \hbar c k - \frac{\hbar}{2i}\Gamma\right)^{-1} \\ &\times\left\{1 - \exp\left[\frac{it}{\hbar}\left(E_0 - E - \hbar c k + \frac{\hbar}{2i}\Gamma\right)\right]\right\} \end{aligned} \tag{30}$$

The summation over k may be replaced by an integral, and provided that the line width Γ is small compared to the frequencies involved, Ea. (30) may be written (Ref. 7 and 10):

$$-i\,\frac{\hbar}{2}\,\Gamma = \left(\frac{e}{mc}\right)^2 \frac{\hbar c}{2(2\pi)^3}\int_0^\infty dk\,k\int d\Omega \sum_{\alpha,E} <\psi_0|D_\alpha^+(\mathbf{k})|\psi_E><\psi_E|D_\alpha^-(\mathbf{k})|\psi_0>$$

$$\times\left[\frac{P}{E_0 - E - \hbar c k} - i\pi\,\delta\,(E_0 - E - \hbar c k)\right] \qquad (31)$$

P means the principal value with respect to the integration over k. Equation (31) clearly shows that Γ is complex:

$$\Gamma = \Gamma_1 + i\Gamma_2 \qquad (32)$$

The real part Γ_1 determines the line width and the imaginary part the line shift. Using the fact that the ψ_E form a complete set, it is easy to see from Eq. (31) that the line shift Γ_2 is given by:

$$\Gamma_2 = \frac{e^2}{m^2 c}(2\pi)^{-3}\sum_\alpha P\int_0^\infty dk\,k\int d\Omega <\psi_0|D_\alpha^+(\mathbf{k})\,(E_0 - H - \hbar c k)^{-1}\,D_\alpha^-(\mathbf{k})|\psi_0> \qquad (33)$$

where the operator H is given by Eq. (4). The line width Γ_1 is obtained from Eq. (31) as:

$$\Gamma_1 = \frac{e^2}{m^2 c}\,\frac{\pi}{(2\pi)^3}\int_0^\infty dk\,k\int d\Omega \sum_{\alpha,E} <\psi_0|D_\alpha^+(\mathbf{k})|\psi_E><\psi_E|D_\alpha^-(\mathbf{k})|\psi_0>\,\delta\,(\hbar c k - E_0 + E) \qquad (34)$$

It is clearly seen that no contribution towards the integral (34) arises if $E_0 - E < 0$. To permit extension of the k integration over the whole range, the step function defined by:

$$S(\hbar c k) = \begin{cases} 1 & \text{if } k > 0 \\ 0 & \text{if } k < 0 \end{cases} \qquad (35)$$

is introduced, together with the integral representation:

$$S(h c k) = \lim_{\epsilon = 0}\frac{1}{2\pi i}\int_{-\infty}^{+\infty} dS\,\frac{e^{ick\hbar S}}{S - i\epsilon} \qquad (36)$$

Inserting this last expression into Eq. (34) and interchanging the integration over k and S, it is possible to integrate over k without restriction and obtain:

$$\Gamma_1 = \left(\frac{e}{m\hbar}\right)^2 (2\pi c)^{-3} \frac{1}{2i} \lim_{\epsilon=0} \int_{-\infty}^{+\infty} dS\,(S - i\epsilon)^{-1} \int d\Omega \sum_{\alpha} \langle\psi_0 | D_\alpha^+(E_0 - H)\, e^{iS(E_0-H)} D_\alpha^- | \psi_0\rangle \tag{37}$$

The operators $D_\alpha^\pm$ in expression (37) are defined in the following way

$$\begin{aligned} D_\alpha^- = {} & \exp\left[-\frac{i}{\hbar c}(E_0 - H)\,\mathbf{e}_k \cdot \left(\mathbf{R}_S - \frac{\mu}{M_1}\mathbf{R} + \mathbf{r}_1\right)\right] \mathbf{e}_k^{(\alpha)} \cdot \mathbf{p}_1 \\ & + \exp\left[-\frac{i}{\hbar c}(E_0 - H)\,\mathbf{e}_k \cdot \left(\mathbf{R}_S + \frac{\mu}{M_2}\mathbf{R} + \mathbf{r}_2\right)\right] \mathbf{e}_k^{(\alpha)} \cdot \mathbf{p}_2 \end{aligned} \tag{38}$$

$$\begin{aligned} D_\alpha^+ = {} & \mathbf{e}_k^{(\alpha)} \cdot \mathbf{p}_1 \exp\left[\frac{i}{\hbar c}\,\mathbf{e}_k \cdot \left(\mathbf{R}_S - \frac{\mu}{M_1}\mathbf{R} + \mathbf{r}_1\right)(E_0 - H)\right] \\ & + \mathbf{e}_k^{(\alpha)} \cdot \mathbf{p}_2 \exp\left[\frac{i}{\hbar c}\,\mathbf{e}_k \cdot \left(\mathbf{R}_S + \frac{\mu}{M_2}\mathbf{R} + \mathbf{r}_2\right)(E_0 - H)\right] \end{aligned} \tag{39}$$

The unit vectors $\mathbf{e}_k$ and $\mathbf{e}_k^{(\alpha)}$ have already been defined, and the exponentials are defined by

$$\exp\left[\frac{i}{\hbar c}\,\mathbf{e}_k \cdot \mathbf{r}\,(E_0 - H)\right] = \sum_{n=0} \frac{1}{n!}\left(\frac{k}{\hbar c}\,\mathbf{e}_k \cdot \mathbf{r}\right)^n (E_0 - H)^n \tag{40}$$

and

$$\exp\left[-\frac{i}{hc}(E_0 - H)\,\mathbf{e}_k \cdot \mathbf{r}\right] = \sum_{n=0} \frac{1}{n!}(E_0 - H)^n \left(\frac{i}{\hbar c}\,\mathbf{e}_k \cdot \mathbf{r}\right)^n \tag{41}$$

To conclude this section a formula for the line shape will be worked out. From Eq. (29) it is known that the probability amplitude for finding a photon with momentum $\mathbf{k}$ and state of polarization α, the particle system being in state ψ_E, is at $t = \infty$:

$$b_\alpha(E, \mathbf{k}, \infty) = -\frac{e}{mc}\left(\frac{\hbar c}{2V}\right)^{1/2} k^{-1/2} < \psi_E | D_\alpha^-(\mathbf{k}) | \psi_0 > \left(E - E_0 + \hbar c k - \frac{\hbar}{2i}\Gamma\right)^{-1} \tag{42}$$

To find the particle system in the following state:

$$\psi_F = V^{-1/2} e^{i\mathbf{K}_S \cdot \mathbf{R}_S + i\mathbf{K}\cdot\mathbf{R}} \zeta_0(\mathbf{r}_1)\, \zeta_0(\mathbf{r}_2) \tag{43}$$

representing a physical situation in which system 1 and system 2 are in their respective ground states, while the relative motion as well as the center-of-mass motion are in definite plane-wave states, according to Eq. (28) is:

$$< \psi_F | \phi_\alpha > = \sum_E b_\alpha(E, \mathbf{k}, \infty) < \psi_F | \psi_E > \tag{44}$$

The probability of a spontaneous emission of a photon into the frequency range between k and $k + dk$ irrespective of both the center-of-mass motion and the relative motion is then given by:

$$\begin{aligned} P &= \int d^3 K_S\, d^3 K\, d\Omega \sum_\alpha |< \psi_F | \phi_\alpha >|^2 \\ &= \frac{e^2}{m^2 c} \frac{\hbar k}{2(2\pi)^3} \left| \left\langle \psi_F \middle| \left(H - E_0 + hck - \frac{\hbar}{2i}\Gamma\right)^{-1} D_\alpha^-(\mathbf{k}) \middle| \psi_0 \right\rangle \right|^2 \end{aligned} \tag{45}$$

Eq. (45) is the final expression for the line shape. Eq. (33), (37) and (45) form the basis of the theory.

III. DISCUSSION

Neglecting the electrostatic interaction energy $\phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R})$ and the photon recoil, the latter by simply omitting the dependence of $D_\alpha^\pm$ on $\mathbf{R}_S$ and $\mathbf{R}$, Eq. (37) for the line width goes directly over into the well-known Weisskopf-Wigner formula for the natural line width for a decay into the ground state:

$$\Gamma_1 = \sum_n w_{ln} \tag{46}$$

where w_{ln} is the transition probability from level l to level n and the sum runs over all lower levels. It is not surprising that our formulas are not applicable to cases where a radiative transition takes place into an unstable level since the fact that a subsequent photon emission can occur, in itself broadens the line and this possibility has not been taken into account in our calculations, two photon amplitudes having been neglected throughout. Incorporating recoil does not change the result (Eq. 46), but the frequencies are shifted by the Doppler effect. In conclusion we wish to show that formula (45) for the line shape can be cast into a form similar to the Fourier integral formula for computing line contours (Ref. 9).

Starting with the identity:

$$\frac{1}{H-a} D = D \frac{1}{H-a} + \frac{1}{H-a} [D, H] \frac{1}{H-a} \tag{47}$$

holding between any two operators H and D ($[D, H] = DH - HD$), the following series may be generated by repeated application of (47):

$$\frac{1}{H-a} D = \sum_{n=0}^{\infty} [D, H]_n \frac{1}{(H-a)^{n+1}} \tag{48}$$

where

$$[D, H]_n = \left[\cdots \left[[D, H], H\right] \cdots, H\right] \tag{49}$$

is the n-fold commutator of D with H. Expressing the operator occurring in the matrix element of Eq. (45) by the series (48) and noting that $H\psi_0 = E_0\psi_0$, it is seen that

$$M = \left\langle \psi_F \middle| \left(H - E_0 + \hbar c k - \frac{\hbar}{2i} \Gamma \right)^{-1} D_\alpha^-(\vec{\mathbf{k}}) \middle| \psi_0 \right\rangle$$

$$= \sum_{n=0}^{\infty} \langle \psi_F | [D_\alpha^-, H]_n | \psi_0 \rangle \left(\hbar c k - \frac{\hbar}{2i} \Gamma \right)^{-(n+1)} \tag{50}$$

But from Heisenberg's equation of motion

$$-i\hbar \left(\frac{d}{dt} D_\alpha^- \right)_{t=0} = [H, D_\alpha^-] \tag{51}$$

it follows that

$$[D_\alpha^-, H]_n = (i\hbar)^n \left(\frac{d^n}{dt^n} D_\alpha^- \right)_{t=0} \tag{52}$$

so that the series (50) goes over into:

$$M = \frac{1}{i\hbar} \sum_{n=0}^{\infty} \left\langle \psi_F \middle| \left(\frac{d^n}{dt^n} D_\alpha^- \right)_{t=0} \middle| \psi_0 \right\rangle \frac{(-1)^{n+1}}{\left(i c k - \frac{1}{2} \Gamma \right)^{n+1}} \tag{53}$$

noting that

$$\frac{1}{n!} \int_0^\infty t^n e^{(ick - ½\Gamma)t} \, dt = \left(i c k - \frac{1}{2} \Gamma \right)^{-(n+1)} \tag{54}$$

one may write

$$M = -\frac{1}{i\hbar} \int_0^\infty dt \, e^{(ick-½\Gamma)t} \sum_{n=0}^{\infty} t^n \frac{1}{n!} \left\langle \psi_F \middle| \left(\frac{d^n}{dt^n} D_\alpha^- \right)_{t=0} \middle| \psi_0 \right\rangle \tag{55}$$

which may be written

$$M = -\frac{1}{i\hbar} \int_0^\infty dt \exp \left[\left(i c k - \frac{1}{2} \Gamma \right) t \right] \langle \psi_F | D_\alpha^-(-t) | \psi_0 \rangle \tag{56}$$

Taking the square of (56), after a few rearrangements:

$$|M|^2 = \frac{1}{\hbar^2} \int_0^{\infty} dt \int_{-\infty}^{t} dt' \exp\left[-ickt' + \frac{1}{2}\Gamma(t'-2t)\right] <\psi_F|D_\alpha^-(t'-t)|\psi_0><\psi_0|D_\alpha^+(t)|\psi_F> \tag{57}$$

It can easily be shown that Eq. (57) goes over into a formula first given by Anderson (Ref. 11) provided a statistical average is taken over the initial states ψ_0 and a summation over all possible final states. In this case one may write with the help of the density matrix ρ of the initial states:

$$<\psi_F|D_\alpha^-(t'-t)|\psi_0><\psi_0|D_\alpha^+(t)|\psi_F> = \mathrm{Tr}\ [\rho\ D_\alpha^+(0)\ D_\alpha^-(t')] \tag{58}$$

Inserting this into Eq. (57), integrating by parts, and neglecting Γ with respect to $c\,k$, it is possible to arrive at

$$|M|^2\ \alpha \int_{-\infty}^{+\infty} dt\ e^{-ickt}\ \mathrm{Tr}\ [\rho\ D_\alpha^+(0)\ D_\alpha^-(t)] \tag{59}$$

which is the formula of Ref. (11).

REFERENCES

1. W. Weisskopf, *Uspechi fiz. Nauk., 13:* 596 (1933); H. Lorentz, *Proc. Amsterdam Aca. Sci., 8:* 591 (1906).

2. A. Unsöld, *Vjschv. astr. Ges., 78:* 213 (1943).

3. H. Margenau, W. Watson, *Rev. Mod. Phys., 8:* 22 (1932).

4. H. Kuhn, *Phil. Mag. 18:* 987 (1934); M. Kulp, *Zeit. f. Phys., 79:* 495 (1932); *87:* 245 (1933).

5. H. Margenau, M. Lewis, *Rev. Mod. Phys., 31:* 569 (1959); R. G. Breene, *Rev. Mod. Phys., 29:* 94 (1957).

6. N. F. Mott, H. S. W. Massey, *The Theory of Atomic Collisions*, 2nd Edition, Oxford at the Clarendon Press, 1949; Chapter VIII.

7. V. Weisskopf, E. Wigner, *Zeit. f. Phys., 63:* 54 (1930); *65:* 18 (1930).

8. I. I. Sobel'man, *Uspechi fiz. Nauk., 54:* 551 (1954).

9. S. Bloom, H. Margenau, *Phys. Rev. 90:* 791 (1953).

10. W. Heitler, *The Quantum Theory of Radiation*, 3rd Edition, Oxford at the Clarendon Press, 1954; p. 183.

11. P. W. Anderson, *Phys. Rev., 76:* 647 (1949).